

Testing and Evaluation of Multifunctional Smart Coatings

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ABSTRACT

A smart coating system, based on pH sensitive microcontainers (microparticles and microcapsules) has been developed. Various corrosion inhibitors have been encapsulated and incorporated into commercial and formulated coatings to test the functionality imparted on the coating by the incorporation of the inhibitor microcontainers. Coated carbon steel and aluminum alloy panels were tested using salt immersion, salt fog, and coastal atmospheric exposure conditions. This paper provides the details on coating sample preparation, evaluation methods, as well as test results of the inhibiting function of smart coatings.

INTRODUCTION

The development of a smart multifunctional corrosion-protective coating system, based on a pH-sensitive delivery system, has evolved significantly over the last few years¹⁻⁴. This effort has resulted in a coating with pH-sensitive microcontainers that can incorporate corrosion indicators, corrosion inhibitors, and self-healing agents to achieve the desired functionalities of early corrosion detection, controlled release of corrosion inhibitor(s), and self-healing of mechanical damage. One important function of the smart coatings is corrosion protection using inhibitor delivery systems. This effort is driven by the need for environmental compliance in protective coating without sacrificing performance.

Progressively stricter regulations on limiting or eliminating certain corrosion inhibitors and reducing the amount of volatile organic compounds (VOCs) have motivated recent research efforts on new corrosion inhibitors and coating formulation development. Some of the new inhibitor chemistries exhibit excellent corrosion protection, such as organic inhibitors that form insoluble metal complexes or water soluble inhibitors that provide quick response at initiation of corrosion, but their incorporation into coatings has been difficult due to their high reactivity with resin systems, or high solubility that lead to blistering and leaching. Smart coatings with pH sensitive microcontainers can be used to overcome these challenges by isolating the inhibitor from the environment through encapsulation.

Various corrosion inhibitors have been encapsulated into pH sensitive microcontainers and incorporated into coating systems for carbon steel and aluminum alloy protection. This paper provide the details on coating sample preparation, evaluation methods, as well as test results of the inhibiting function of smart coatings.

EXPERIMENTAL PROCEDURE

Five coating systems were tested with different encapsulated corrosion inhibitors, as shown in Table 1. For carbon steel protective coating systems, zinc-rich primer, solvent based epoxy, and water based coatings are tested. Epoxy system is tested also for aluminum 2024 substrate.

Table 1: Substrate and Coating Systems Tested with Different Encapsulated Corrosion Inhibitors

Substrate	Coating	Encapsulated Inhibitor(s)	Test Performed
Carbon Steel	Inorganic Zinc Primer	8-HQ Water-soluble inhibitors Inorganic compound	6000 Hours Salt Fog Atmospheric exposure
Zinc Phosphated Carbon Steel	Epoxy System	8-HQ PPA	10 Days Hot Salt Water Immersion
Carbon Steel	Thin Film Epoxy Primer	Inorganic inhibitor Water-soluble inhibitor Combination of both	Atmospheric exposure
Carbon Steel	Water-Based Acrylic	Water-soluble inhibitor Flash rust inhibitor Flash rust inhibitor/8-HQ	1000 Hours Salt Fog
Aluminum 2024	Epoxy-Amine System	8-HQ 2-MBT Water-soluble inhibitors Hybrid encapsulated 2-MBT CMBT/2-MBT	2000+ Hours Salt Fog

Inorganic zinc primers are the primary protective coating for carbon steel at marine/coastal environments such as NASA's Kennedy Space Center (KSC). Its excellent protection relies on proper surface preparation, poor adhesion and performance can result when the carbon steel substrate is not able to be prepared properly as in the cases of hard to reach areas and repairs. Zinc phosphate pre-treated carbon steel with an epoxy coating system is also used for is a desirable form of protection in certain uses and environments. This system is similar to that of the inorganic zinc primer in that a form of zinc is the main corrosion protection of the carbon steel, but unlike zinc primer, zinc phosphate alone is not enough to protect the carbon steel from corrosion.

Thin film epoxy primers are used in a production setting where short recoat times are desirable. Even though these coatings already provide good adhesion and corrosion resistance, their performance could further be improved in certain environments. Next generation corrosion protection of carbon steel involves the use of water-based coatings due to their ease of use and significantly lower impacts on the environment. Their use is ready to expand if their corrosion protection level can rival that of solvent-based systems.

Protection of aluminum alloy is mainly focused on the development of chromate-free epoxy coating systems for aerospace applications.

Inorganic Zinc Primer on Carbon Steel

The first test of inorganic zinc primer was to determine which microcontainer would give the best adhesion of inorganic zinc on non-optimally prepared carbon steel substrate. The carbon steel substrate used for this test was a 3 in. x 5 in. Q-panel with a Type S ground surface purchased from Q-Labs. Its ground surface has a profile of 0.5-1 mil. The inorganic zinc coating used for this testing was Zinc Clad II Plus supplied by Sherwin Williams. The testing of the coated panels was carried out in a QFOG CCT-1100 salt fog chamber, purchased from Q-Labs, running according to ASTM B117⁵. Panels were placed in the chamber and removed after 6000 hours of continuous testing for evaluation.

After determining the three candidates that gave the best adhesion results in the salt fog chamber, they were used for further testing. The three candidates chosen for further testing were 8-Hydroxyquinoline (8-HQ) microcontainers, a combination of organic encapsulated water-soluble inhibitors, and an inorganic compound. The next test was designed to simulate an inorganic zinc coating that needs to be repaired

due to a compromised area. A large 6 in. x 12 in. carbon steel panel was spray coated with the same inorganic zinc coating used in the previous test, Zinc Clad II Plus. A middle portion of the panel was then cleaned away to simulate a small area of repair. This section was then repaired with various coatings, some containing microcontainers, and then were tested at NASA's Beach Corrosion Test Site under atmospheric exposure conditions to compare the performance of the repaired areas.

Epoxy Coating on Zinc Phosphate Pre-Treated Carbon Steel

Zinc phosphate pre-treated carbon steel panels were used in this test and provided a thin layer of a zinc compound directly on the carbon steel similar to a galvanic zinc layer. An epoxy coating was then applied over this pre-treatment. The epoxy coating was a two-component solvent based formulation with a low molecular weight epoxy resin solution mixed with an isocyanate hardener. It was applied to the substrate using a #36 formed rod purchased from Gradco. After coating, the panels were cured at 170°C for 20 minutes. Panels were then scribed with an "X" pattern by hand using a template. The completed panels were tested for 10 days immersed in a heated (55°C) 5% sodium chloride (NaCl) solution.

Thin Film Epoxy Primer with Polyurethane Top Coat on Carbon Steel

For this test, the substrate used was a 3 in. x 6 in. carbon steel panel with no pre-treatment. The thin film epoxy primer was spray applied to the carbon steel resulting in a dry film thickness of 1-2 mils. The epoxy primer was then top-coated with a polyurethane. Microcontainers with corrosion inhibitors were incorporated into the epoxy primer before it was spray applied for additional corrosion protection. There were no noticeable issues with the incorporation of the microcontainers. Four different coatings were made to see which microcontainers were the most effective: one with no microcontainers, a second with organic encapsulated inorganic inhibitor, a third with organic encapsulated water-soluble inhibitor, and a fourth with a combination of both. The completed coatings were then placed at NASA's Beach Corrosion Test Site for atmospheric corrosion resistance testing.

Water-Based Acrylic Coating on Carbon Steel

This test was designed to use a water-soluble inorganic and flash rust inhibitors to improve the performance of a water-based coating. The carbon steel substrate used for this test was a 3 in. x 5 in. Q-panel with a Type S ground surface. The water-based coating selected for this test was an acrylic, Carbocrylic 3359 supplied by Carboline. Two coats of the coating were used with the bottom coat incorporating the microcontainers for testing. The top coat was just the Carbocrylic with no additional additives and was used on all systems. The microcontainers were incorporated into the coating with no noticeable issues. The coating was applied to the substrate using the #80 formed rod. The coating was allowed to fully cure for three weeks before being tested. A single vertical scribe, in the horizontal center of the panel, was done with a hand scribe tool and a ruler. The completed coatings were then placed in the salt fog chamber and tested according to the ASTM B117⁵ standard for 1000 hours.

Epoxy-Amine Coating for Aluminum Alloy

The aluminum substrate used for this test was a 3 in. x 6 in. panel of aluminum 2024-T3 bare supplied by Tri-Tech Metals. An epoxy-amine coating system was selected for this test as a model coating for the protection of aluminum alloy and to test the effectiveness of the added inhibitor microcontainers for corrosion protection. The epoxy-amine coating is a 2-component solvent-based formulation using a bisphenol-A epoxy resin mixed with a polyamine/amine functional polyamide resin blend with an added silane to enhance adhesion. Pigments in the coating include titanium dioxide, carbon black, and magnesium oxide with a solvent blend of butanol, xylenes, and parachlorobenzotrifluoride.

The substrate was prepped by abrading the surface to aid in adhesion and cleaning it using soap and warm water followed by an acetone wash and forced air drying. After prepping the substrate, the coating was applied using the #80 formed rod. The coating was allowed to cure for 7 days before being tested.

Scribes in the shape of an “X” were made using a computerized engraving machine to ensure consistency from one panel to the next.

Microcontainers with corrosion inhibitors were incorporated into the epoxy-amine coating before it was applied for additional corrosion protection. Different coatings were made with various types of microcontainers loaded with various inhibitors to compare their corrosion protection performance. There were no noticeable issues with the incorporation of the microcontainers. The completed coatings were then placed in a salt fog chamber and tested according to the ASTM B117⁵ standard.

RESULTS

Figure 2 shows a panel from each of the best performing inorganic zinc primer systems versus that of a control after being tested in the salt fog chamber for 6000 hours. These panels were used to test the effect of encapsulated inhibitor on the adhesion of inorganic zinc primer on carbon steel with minimum surface preparation. The control (Fig. 2A) has many areas where a loss of adhesion has occurred and blisters with corrosion of the substrate have formed or the zinc in the primer itself has begun to corrode, as evidenced by the white zinc oxide on the panel. Coatings containing encapsulated inhibitors (Fig. 2B, C, and D) show no signs of any loss of adhesion and contain no coating blistering or significant zinc corrosion.

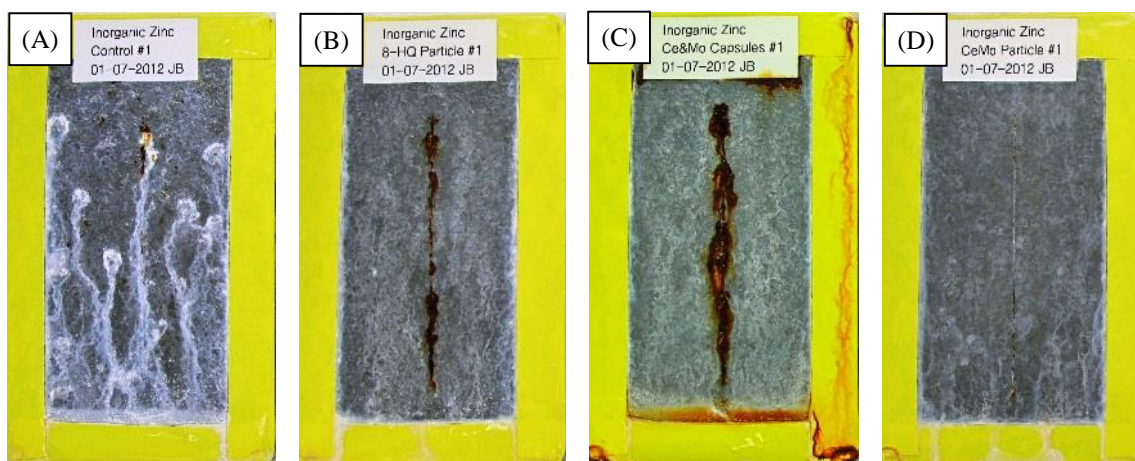


Figure 2: Carbon steel coated with inorganic zinc coating A) containing no micro containers, B) containing encapsulated 8-HQ, C) containing a combination of encapsulated water-soluble inhibitors, and D) containing an inorganic compound, tested for 6000 hours according to ASTM B117

Figure 3 shows panels from each of the five systems tested in the second study of inorganic zinc primer that involves coating repair. These panels have been in atmospheric test conditions for 18 months with testing still ongoing. Two controls were selected for this test, one is an epoxy-mastic coating currently being used to repair inorganic zinc (Fig. 3A) and the other is repaired with inorganic zinc primer containing no encapsulated inhibitor (Fig. 3B). Epoxy-mastic coating is performing better than expected showing no loss of adhesion or corrosion but is chalking and fading due to UV degradation. Inorganic zinc primer control is not showing any loss of adhesion but has zinc corrosion product appearing as evidenced by the white spots in the repaired section of the coating. The coating containing encapsulated 8-HQ (Fig. 3C) is performing very well showing no adhesion loss or zinc corrosion. Coatings containing encapsulated water-soluble inhibitors (Fig. 3D) and an inorganic compound (Fig. 3E) are performing similarly with no loss of adhesion but are showing some zinc corrosion.

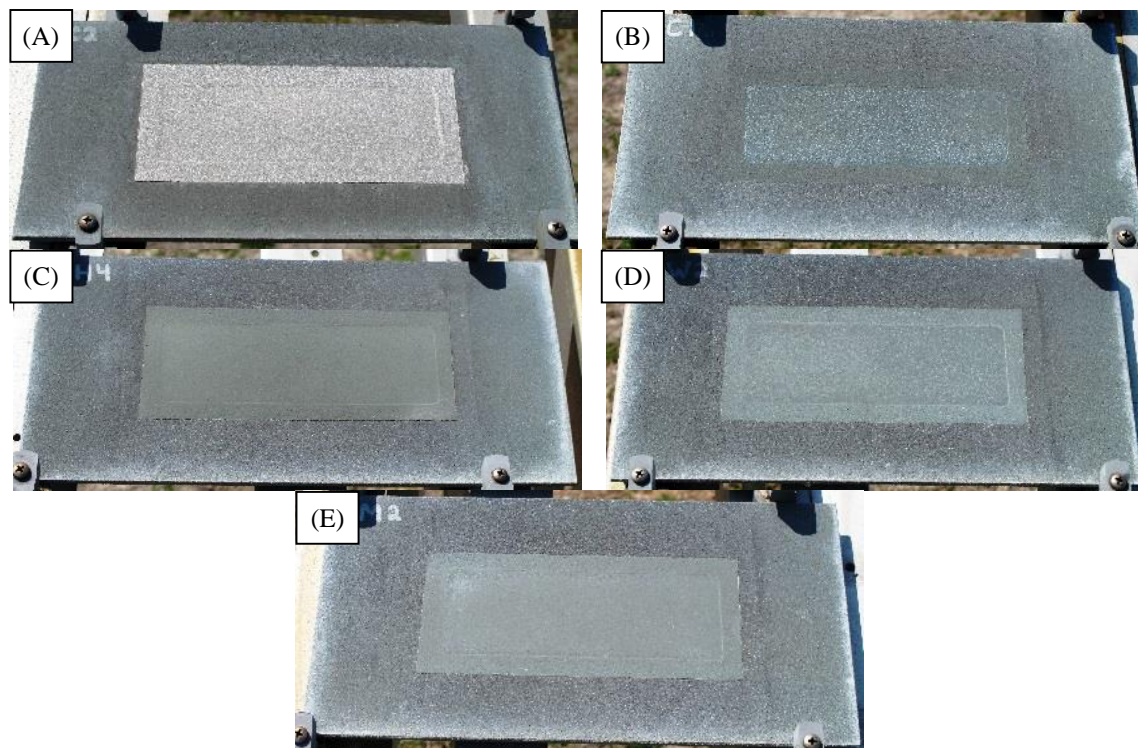


Figure 3: Carbon steel coated with inorganic zinc coating and then patched with A) epoxy-mastic coating (currently used) B) inorganic zinc control, C) inorganic zinc containing encapsulated 8-HQ, D) inorganic zinc containing a combination of encapsulated water-soluble inhibitors, and E) inorganic zinc containing an inorganic compound, tested for 18 months at the Beach Corrosion Test Site

Figure 4 shows zinc phosphate pre-treated carbon steel panels coated with an epoxy coating with and without microcontainers tested for 10 days immersed in a hot 5% NaCl solution (55°C). After testing is complete and the panels are dry, the coating is tape pulled to measure creep from scribe. The control coating (Fig. 4A) has a creep from scribe of 1.5 mm. A coating containing encapsulated 8-HQ (Fig. 4B) has a creep from scribe of just 0.1 mm. This significant decrease in creep from scribe compared to control shows the 8-HQ microcontainers provide protection from corrosion and help to maintain coating adhesion around the scribe. Figure 4C shows the coating containing encapsulated Phenylphosphonic Acid (PPA) with a creep from scribe of 1.0 mm providing some corrosion protection but not a significant amount as seen with 8-HQ.

An increase in corrosion protection was observed when 8-HQ microcontainers are combined with either the inorganic zinc primer or in the epoxy coating applied over zinc phosphate. Since zinc is the common element between these two, there appears to be a synergistic effect to aid in protecting carbon steel from corrosion when 8-HQ and zinc are combined. It is well known that 8-HQ and zinc will form a metal complex, and it is likely that this metal complex has contributed to the corrosion protection properties of the coatings that leads to these results.

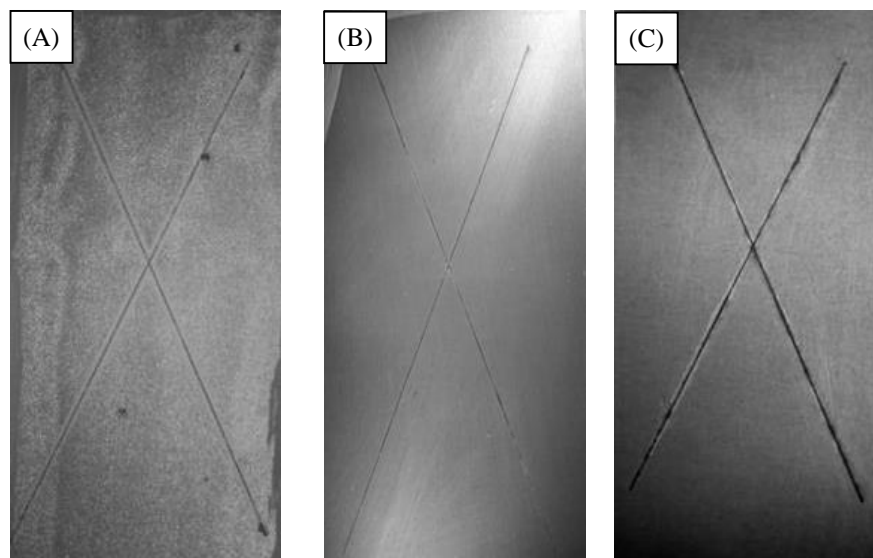


Figure 4: Zinc phosphate pre-treated carbon steel coated with epoxy coating A) control, B) containing encapsulated 8-HQ, and C) containing encapsulated PPA, tested for 10 days immersed in a hot 5% NaCl salt solution

Figure 5 shows a carbon steel panel coated with one of four thin film epoxy primer systems tested after both 6.5 months and 17.5 months in atmospheric conditions. The control coating (Fig. 5A) shows high levels of corrosion from the scribe after 6.5 months with significant corrosion from the scribe moving upward over the rest of the panel after 17.5 months. This is also leading to significant amounts of corrosion under the coating causing it to delaminate and fall off. A coating containing encapsulated inorganic inhibitor (Fig. 5B) shows less corrosion from the scribe at the 6.5 month and less corrosion spreading up the panel from the scribe at 17.5 months. Fig. 5C shows a coating containing an encapsulated water-soluble inhibitor performs the best in terms of the corrosion being limited to just creep from scribe with no other significant amounts of corrosion on the panel. Similarly, the coating containing a combination of these encapsulated inhibitors (Fig. 5D) performs the best in terms of creep from scribe corrosion but shows corrosion around the rest of the panel. These last three coating systems (Fig. 5B, C, and D) show improvement over the control coating displaying the ability of encapsulated inhibitors to improve the corrosion protection of a thin film epoxy primer.

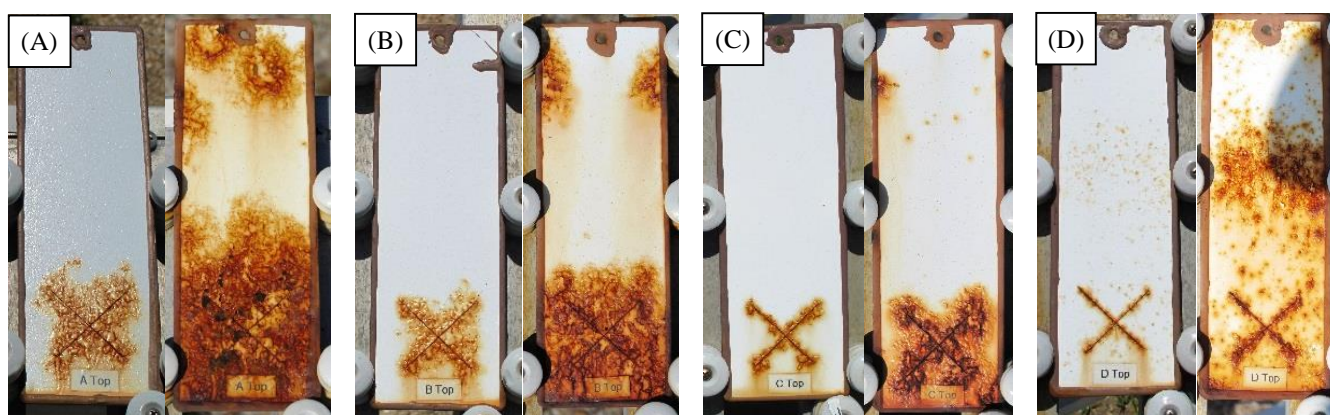


Figure 5: Carbon steel coated with thin film epoxy coating, A) control, B) containing encapsulated inorganic inhibitor, C) containing encapsulated water-soluble inorganic inhibitor, D) containing a combination of B and C, top-coated with a polyurethane then tested for 6.5 months (left) and 17.5 months (right) at NASA's Beach Corrosion Test Site

Figure 6 shows carbon steel panels from each of the best performing microcontainers tested in a water-based acrylic coating versus that of a control after being tested in a salt fog chamber for 1000 hours. The control coating (Fig. 6A) shows blistering and corrosion from the scribe spreading across the panel. The other three coatings containing encapsulated water-soluble inhibitor (Fig. 6B), with flash rust inhibitor (Fig. 6C), and with a combination of flash rust inhibitor and 8-HQ (Fig. 6D) all perform similar with only small amounts of blistering and corrosion occurring around the scribe. These coatings show significant improvement over the control coating displaying the ability of the encapsulated inhibitors to improve the corrosion protection of a water-based acrylic coating.

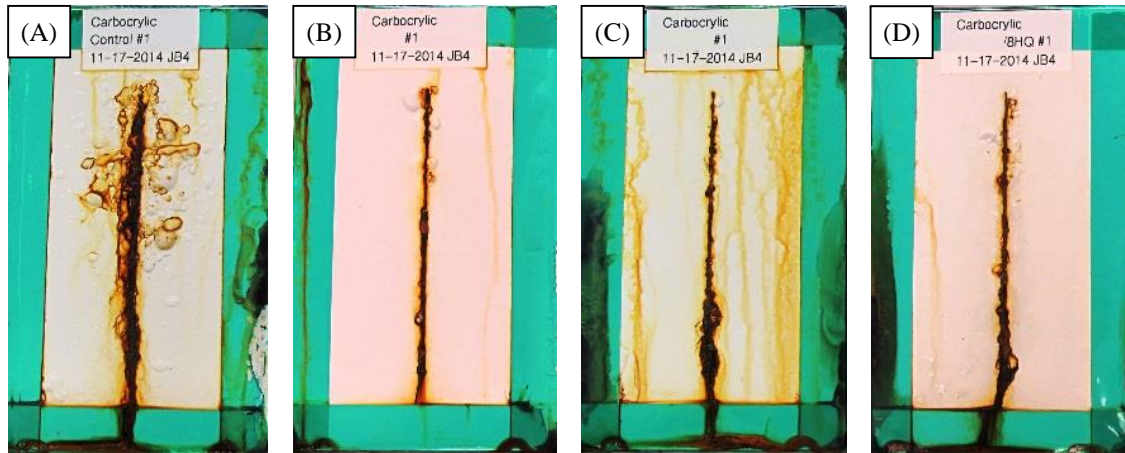


Figure 6: Carbon steel coated with water-based acrylic coating A) control, B) containing encapsulated water-soluble inhibitor, C) containing encapsulated flash rust inhibitor, and D) containing a combination of encapsulated flash rust inhibitor and 8-HQ, tested for 1000 hours according to ASTM B117

Figure 7 shows aluminum 2024 panels coated with epoxy-amine coating containing microcontainers compared to a control panel after being tested in the salt fog chamber to 2000 hours. The control coating (Fig. 7A) shows various signs of corrosion with a discolored, darkened scribe that is no longer shiny like it was before testing. There are also local spots of corrosion in the scribe as evidenced by the white aluminum oxide corrosion product. It is also beginning to blister away from the scribe. The coatings containing encapsulated 8-HQ, 2-Mercaptobenzothiazole (2-MBT), and water-soluble inhibitor (Fig. 7B, C, and D respectively) all perform similarly with discoloration of the scribe, local spots of corrosion in the scribe, and blistering beginning to spread in the coating from the scribe. The best performers are the encapsulated water-soluble inhibitor (Fig. 7E) and the hybrid encapsulated 2-MBT (Fig. 7F) with the encapsulated water-soluble inhibitor just having some discoloration in the scribe with a few local spots of corrosion. The hybrid encapsulated 2-MBT has excellent performance with only slight discoloration of the scribe, and in some areas, it's still shiny. The last coating (Fig. 7G) contains an encapsulated mixture of different forms of 2-MBT. It also has the discoloration in the scribe along with local areas of corrosion, but there is no blistering of the coating. Instead, it has local areas of corrosion away from the scribe and was the only system to do this.

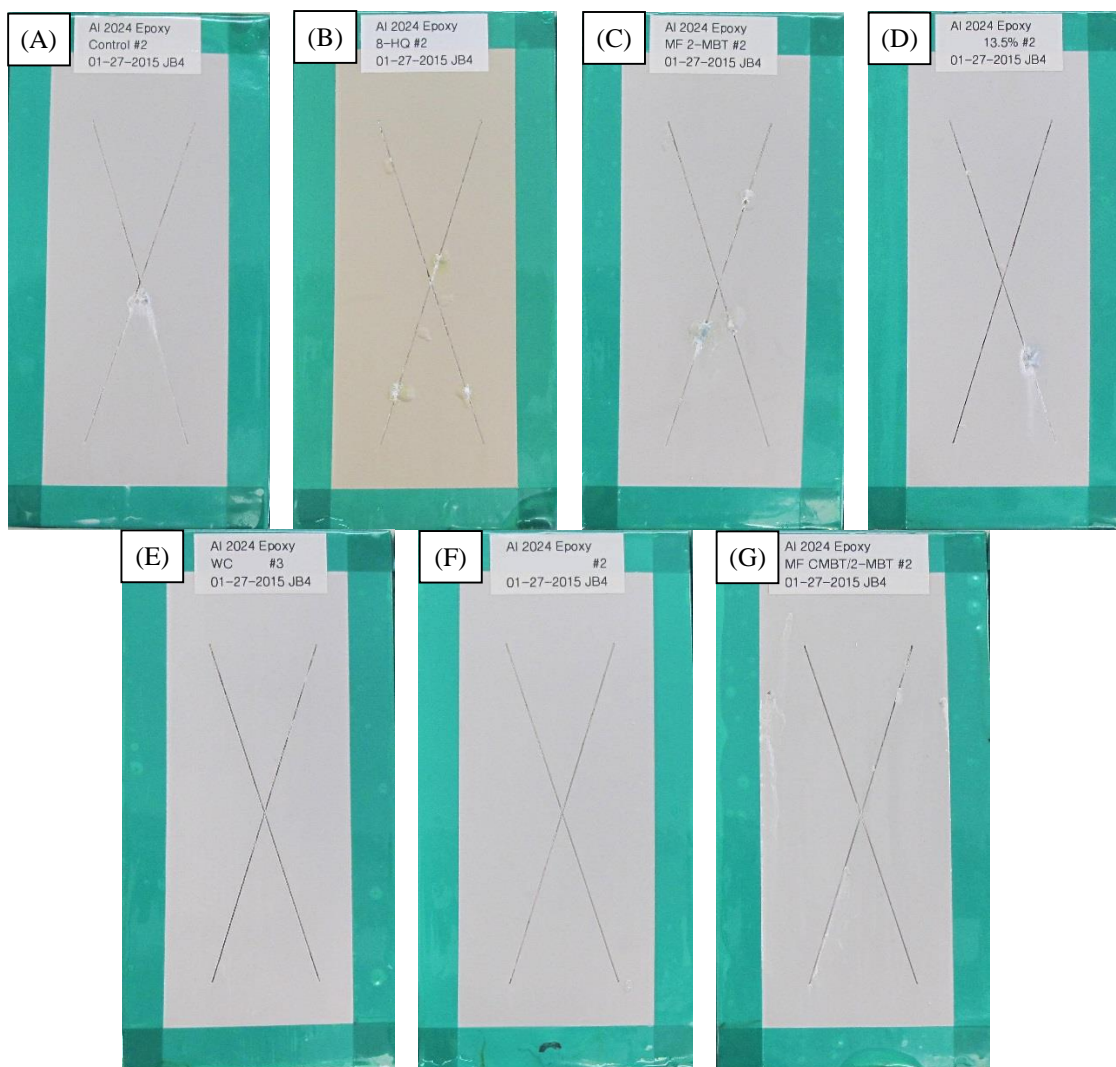


Figure 7: Epoxy-Amine coating tested on Aluminum 2024-T3 bare, A) containing no microcontainers, B) containing 8-HQ microcontainers, C) containing 2-MBT microcontainers, D,E) containing encapsulated water-soluble inhibitors, F) containing hybrid encapsulated 2-mecaptobenzothiazole, G) encapsulated mixture of 2-MBT, tested to 2000 hours according to ASTM B117

The best performing coatings containing encapsulated inhibitors for a given substrate are summarized in Table 8. For an inorganic zinc primer on carbon steel or epoxy system on zinc phosphate pre-treated carbon steel, the encapsulated 8-HQ has shown the ability to protect the carbon steel substrate likely through its interaction with zinc in the system. Thin film epoxy primer containing encapsulated water-soluble inhibitor and its combination with an encapsulated inorganic inhibitor have both shown the ability to enhance the protection of carbon steel over control in atmospheric conditions. The encapsulated flash rust inhibitor and water-soluble inhibitor have both significantly improved the corrosion protection of a water-based coating for carbon steel resulting in 1000 hours of salt fog performance. For aluminum alloy protection with an epoxy-amine coating, the encapsulated water-soluble inhibitor and hybrid encapsulated 2-MBT have both demonstrated the ability to protect the aluminum panel away from the scribe but with the later even protect the scribe area.

Table 8: Best Performing Encapsulated Corrosion Inhibitors for Each Coating System Tested

Substrate	Coating	Best Performing Encapsulated Inhibitor(s)
Carbon Steel	Inorganic Zinc Primer	8-HQ
Zinc Phosphated Carbon Steel	Epoxy System	8-HQ
Carbon Steel	Thin Film Epoxy Primer	Water-soluble inhibitor Combination of inhibitors
Carbon Steel	Water-Based Acrylic	Water-soluble inhibitor Flash rust inhibitor Flash rust inhibitor/8-HQ
Aluminum 2024	Epoxy-Amine System	Water-soluble inhibitor Hybrid encapsulated 2-MBT

CONCLUSIONS

In summary, a smart coating system, based on pH sensitive microcontainers (microparticles and microcapsules) has been developed. Various corrosion inhibitors have been encapsulated and incorporated into commercial and formulated coatings to test the functionality imparted on the coating by the incorporation of the inhibitor microcontainers. Coated carbon steel and aluminum alloy panels were tested using salt immersion, salt fog, and coastal atmospheric exposure conditions. All the different coating tests performed have shown the versatility of pH-sensitive microcontainers encapsulating various inhibitors to provide corrosion protection for carbon steel and aluminum alloy of various coating systems.

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